Phase Transitions in $Al_{87}Ni_7Nd_6$

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ABSTRACT

The local atomic structure of $Al_{87}Ni_7Nd_6$ amorphous metallic glass was determined upon heating by neutron diffraction and the pair density function (PDF) analysis. Two isotopes of Ni with very different scattering intensities were used (^{58}Ni and ^{60}Ni) to separate the local environment of the transition metal. A distinct pre-peak observed in reciprocal space arises because of chemical clustering of Ni atoms. With increasing temperature the coherence length of this peak increases indicating an enhancement in atomic clustering. In addition, precipitation of Al metal is first observed at 200 ^{o}C with heating. Binary and ternary Al phases form as the temperature increases further to 500 ^{o}C although the majority crystalline phase is Al. The local atomic topology at the intermediate temperatures can be represented with a model that is a combination of the atomic structure at room temperature plus Al.

INTRODUCTION

A group of Al-TM-RE (TM = transition metal, RE = rare earth) metallic glasses with remarkably high Al content (up to 90 at. %) was synthesized independently by He, Poon and Shiflet, and Tsai, Inoue and Masumoto [1, 2]. Previously studied compositions for the Al-TM-RE glass, where TM is a late transition metal such as iron, cobalt or nickel and RE is a rare-earth metal such as yttrium, gadolinium or cerium, include $Al_{87}Ni_5Y_8$, $Al_{90}Fe_5Ce_5$ and $Al_{87}Fe_{8.7}Gd_{4.3}$ [1, 3]. The amorphous phase is formed with an Al content as high as 84 at. % for samples prepared by the magnetron sputtering process and as high as 90 at. % for samples prepared by the melt spinning process. These materials are truly noncrystalline alloys and combine the properties of a metal with the short-range order effects of a glass. They are very homogeneous and lack defects such as grain boundaries and dislocations typical of crystalline materials. The homogeneity and lack of grain boundaries have led to a number of remarkable mechanical and magnetic properties [4].

Earlier neutron and x-ray structural studies of melt spun $Al_{87}Fe_xCe_{10-x}$ alloys revealed a strong interaction in the vicinity of the first coordination sphere of Fe [5, 6]. The Fe-Al bond lengths were found to be anomalously short with a suggested 8 % contraction and a low coordination number, a 45 % reduction from values based on dense-random-packing (DRP) of a hard spheres model. However, the Ce-Al bonds show relatively smaller changes with a 5 % reduction in the bond length and a 13 % reduction in the coordination number from the expected values

based on DRP models. These anomalous changes for the Fe-Al bonds in the amorphous phase indicate a strong interaction between the Fe and Al atoms that may be in response to the increase in the covalency between the ions and a reduction in their metallic character.

Recent neutron structural studies on $Al_{87}Ni_7Nd_6$ using isotopes of Ni and Nd showed that the short range environment of Ni determined by the isotope difference pair density function (DPDF) technique is significantly different from that of Nd giving rise to new topological order [7]. The differences between the two environments are not merely attributed to differences in their atomic size but to their different interactions with Al. In the case of Al-Ni, the coordination is almost the same as the coordination calculated from a DRP model. This is markedly different from the AlFeCe system where a reduced coordination was observed. At the same time, the Ni-Al bond length (2.46 Å) is shorter than expected assuming metallic character of the bond and gives rise to new local topology, similarly to what was observed for the Fe-Al bond in the Al-FeCe alloy. On the other hand, Nd's bonding to Al shows no contraction and gives rise to two different local environments. The majority of Nd-Al pairs are essentially described assuming metallic nature of the bond while a small number of Nd-Al pairs have slightly larger bonds. In addition, the Nd-Al coordination is actually enhanced, 14 pairs for the first pair and 4 for the second pair, not too far off the value of 16.4 calculated from a DRP model.

In this paper, the atomic structure upon heating of the $Al_{87}Ni_7Nd_6$ amorphous alloy using pulsed neutron diffraction is reported. By using isotopes for Ni, ^{58}Ni and ^{60}Ni, the local environment for the transition metal was differentiated. From the atom specific structure function, a strong pre-peak at 1.5 Å^{-1} is identified that changes intensity with Ni isotopic substitution [7]. This is indicative for the presence of chemical short range ordering (CSRO) that is enhanced by the transition metal in this system and less so by the rare earth. The CSRO has been observed in other glass systems and is consistent with good glass forming ability. With increasing temperature, the width of the pre-peak gets narrower indicating an increase in the coherence length. The first phase that appears with heating is Al metal. The Al content increases with temperature. By 500 °C, Al_3Ni, Al_2Nd and Al_4Nd are formed in addition to the Al phase while a fifth phase probably due to a ternary AlNiNd phase is present but its crystal structure was not identified. The local atomic structure of the amorphous metal changes significantly with heating due to the appearance of all phases. It is possible to reproduce the changes by combining the room temperature phase with models of the crystal phases that appear with increasing temperature. As the majority phase is made of Al, most of the changes can be accounted for by adding Al. However, by 500 °C, when several other phases appear, the local structure is already quite complex.

EXPERIMENT

Amorphous ribbons of $Al_{87}Ni_7Nd_6$ were prepared using natural Ni and ^{58}Ni and ^{60}Ni isotopes [8]. The alloy ingots were prepared by arc-melting in an argon atmosphere using nominal amounts for each element. The ribbons were melt-spun in a partial helium atmosphere using a copper wheel (20cm in diameter) with a typical circumferential velocity of 40 m/sec. Typical dimensions were 15 μm thick, 1-2 mm wide and up to several meters long. The melt-spun ribbons were very flexible and could easily be bent in half without fracturing. The high temperature neutron data were collected using the Polaris instrument at ISIS in Rutherford Laboratory, England. Data were collected as a function of temperature and the structure function, S(Q), was Fourier transform to determine the pair density function (PDF). The PDF is a real space repre-

sentation of atomic pair correlations and the analysis provides direct information with regard to the local structure without requiring long-range structural periodicity. It is quite commonly used in the analysis for amorphous systems [9].

The diffraction data were also analyzed using the Rietveld refinement to determine the crystal phases appearing during heating with the crystallization process. The first phase that crystallizes with heating is that of face centered cubic (fcc) Al and its lattice constant, a, is listed in Table 1. The increase in a follows that of Al metal and the values are consistent for both isotopes. For data collected at 500 °C, Al_3Ni with *Pnma* symmetry, Al_3Ni with *Fd-3m* symmetry and Al_4Nd with *Imm2* symmetry are additionally formed. Another potential phase is AlNiNd with *P-62m* symmetry was partially indexed. The phase fractions of the identified phases are as follows: Al ~ 57 %, Al_4Nd ~ 18 %, Al_3Ni ~ 14 %, and Al_2Nd ~ 10 %. These are relative quantities and it should be noted that there is a significant amount of an amorphous phase, although this is not of the same content as the one at room temperature.

Table 1: A list of Al lattice constants for the two isotopes, $Al_{87}{}^{58}Ni_7Nd_6$ and $Al_{87}{}^{60}Ni_7Nd_6$. Al metal is the first phase that appears with crystallization. The relative volume fraction of this phase increases with heating. At 500 °C, the majority phase is that of Al while 4 other phases are present simultaneously.

	Al (Fm$\bar{3}$m)	
Temperature	^{58}Ni (Å)	^{60}Ni (Å)
150 °C		
200 °C	4.0670(7)	4.0686(5)
225 °C	4.0686(5)	4.0709(4)
250 °C	4.0726(4)	4.0742(3)
500 °C	4.1014(2)	4.1034(1)

DISCUSSION

The quenching of the liquid bypasses crystallization and leads to a metastable phase at room temperature that is amorphous where this process is reproducible. With slow cooling, stable crystalline phases will appear and the amorphous phase will never be reached. We investigated the nature of the competing crystalline phases that appear in the temperature range between the liquid and the solid upon heating amorphous ribbons of $Al_{87}Ni_7Nd_6$. Although the phases that appear with heating might be different from the ones that form on cooling, it is experimentally difficult to cool the liquid in a furnace used in the neutron experiment as fast as it is done in a melt spinning process. The structure function shown in Fig. 1 indicates that with increasing temperature, crystalline Al begins to form at about 200 °C. The observed Bragg peaks are assigned to fcc Al while the phase is predominantly amorphous. With further heating, the Bragg peaks get sharper and the Al phase grows at the expense of the amorphous phase. By 500 °C, several phases are formed of binary Al compounds with Ni and Nd as shown in Fig. 2 and their crystal structures have been indexed. This is not a complete transformation to a crystal form as
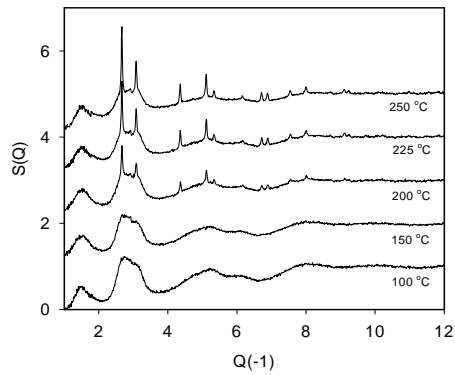
Figure 1: The structure function with increasing temperature of ^{58}Ni. The diffraction peaks are indexed to Al.
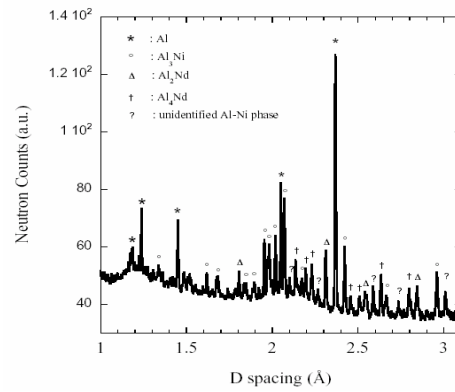

Figure 2: Profile pattern at 500 $^{\circ}$C where several phases have been identified.

the amorphous phase is still quite significant and contributes to the background of the observed spectrum. Another phase was partially indexed that consists of AlNiNd ternary.

The structure functions of Fig. 1 show a distinct pre-peak at ~ 1.5 Å^{-1} at all temperatures. This feature was also observed at room temperature measurements of the same sample carried out at the SEPD instrument of the Intense Pulsed Neutron Source of Argonne National Laboratory. Isotopic substitution with Ni changes the intensity of the pre-peak significantly while isotopic substitution with Nd leads to almost no change in the intensity. This shows that the chemical composition of the pre-peak is primarily made of Ni and its existence indicates some form of chemical clustering. The pre-peak does not disappear with heating but instead the width of peak gets narrower where the coherence length of the chemical clusters increases with heating (Fig. 3).The coherence length at T $\geq$ 500 $^{\circ}$C is not shown because of the multiple crystal phases.

The local structure of the corresponding structure functions is shown in Fig. 4. The first peak consists of three different pairs, Al-Ni, Al-Al and Al-Nd at room temperature. With heating however, as Al metal precipitates out of the amorphous phase, the local structure primarily

Figure 3: Cluster coherence length determined from the pre-peak in the structure function using the ^{58}Ni data.

changes because of the additional Al correlations that are superimposed on the local structure of the amorphous glass. By 500 $^{\circ}$C, the appearance of all crystalline phases gives rise to a complex local structure. Similar changes were observed in Al$_{87}$^{60}Ni$_7$Nd$_6$ ribbons.

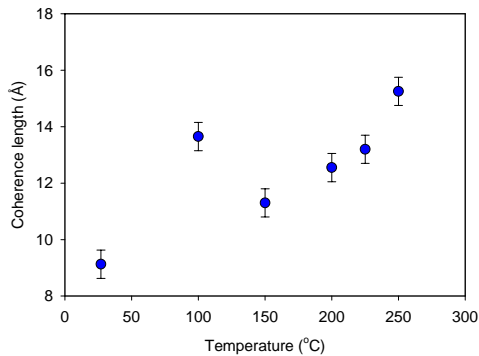Fig. 5 is a model for the local atomic structure at 225 $^{\circ}$C where 5 % of Al phase is estimated to be present. This model is constructed from adding the calculated Al pair density function on room temperature data (completely amorphous) and weighted by the appropriate mass changes and scattering lengths. The split in the first peak is due to the presence of Al as shown in the pair correlation function at the bottom of the figure. Other changes are also observed in the atomic structure that are attrib-

uted to Al. The observed differences can be well understood by considering the fact that the amorphous phase is actually different from the one at room temperature since the Al content is changing with heating. The amount of Al present is small however.
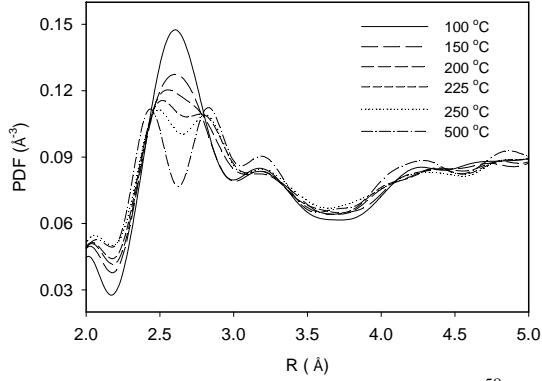

Figure 4: The local atomic structure for $Al_{87}{}^{58}Ni_7Nd_6$ at several temperatures. Above 500 °C, the atomic structure is dominated by the crystalline phases.
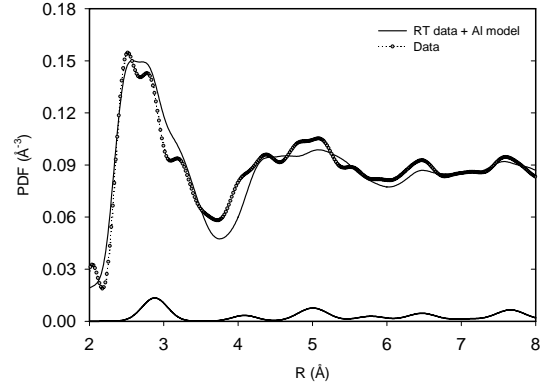

Figure 5: The local atomic structure determined at 225 °C is compared to a model constructed by adding 5 % of Al (shown at the bottom of the figure) to the 27 °C data determined using the SEPD [7].

CONCLUSIONS

The neutron scattering results reported in this paper suggest that chemical clustering persists as the temperature increases that serves as an indication that the Ni clusters expand. The fact that the coherence length increases with temperature is unusual, as the opposite effect would be expected. These clusters could persist in the liquid phase as well. A measurement in the liquid phase was attempted but oxidation of the sample occurred. The appearance of the Al phase has been observed by other methods such as differential scanning calorimetry. At 200 °C, only a few percent of the volume fraction consists of Al. The majority phase is predominantly amorphous. As the temperature increases, the volume fraction increases as well. By 500 °C, four to five other phases are present while about 60 % of the relative volume fraction is Al.

The local environment changes significantly with temperature and with the crystallization of the new phases. For intermediate temperatures where only Al metal crystallizes, the local structure can be modeled by considering only two phases: that of the amorphous metallic glass phase at room temperature and a percent of the Al phase at the particular temperature. This indicates that although some Al precipitates out of the amorphous phase, the atomic topology is predominantly amorphous. Addition of the Al metal phase improves the model and indicates where the changes are occurring in the local atomic topology. However, with the crystallization of the other phases, the local structure is already quite complex as it is a linear combination of the phases present.

ACKNOWLEDGMENTS

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